CHARACTERIZATION OF MARTIN LAKE LIGNITE AND ITS RESIDUES AFTER LIQUEFACTION

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ABSTRACT

Martin Lake, Texas lignite typically gives 90-93% conversion in two-stage thermal/catalytic (T/C) liquefaction and 85-90% conversion in two-stage catalytic/catalytic liquefaction (C/C), as demonstrated at Amoco and at the Advanced Coal Liquefaction Facility in Wilsonville, Alabama. To identify the chemical and physical phenomena that underlie this low conversion, Martin Lake lignite and two of its residues, from C/C runs at Amoco, were analyzed by several analytical methods.

The atomic H/C ratio in the solids went through a minimum from 0.86, to 0.78, to 0.90 as conversion increased from 0%, to 64%, and 89%, respectively. Oxygen (wt.%, dry) was lowest in the high-conversion residue, giving 21.2%, 14.3%, and 11.4% at 0%, 64%, and 89% conversion, respectively. X-ray photoelectron spectroscopy (XPS) showed a similar trend of more carbon-oxygen bonds on the surface of unconverted lignite particles. XPS also showed surface enrichment of Ca and Mg with increase in conversion, whereas bulk Ca and Mg remained a constant fraction of the mineral matter. Carbonyl, aliphatic, and aromatic phenol/ether carbons were converted more rapidly than protonated aromatic, substituted aromatic, or bridgehead aromatic carbons, as shown by ^{13}C NMR. Volatile matter remained quite high, 26% (dry), in the high-conversion residue. Petrographic analysis showed a decrease in vitrinites, near-depletion of liptinites, and a sharp increase in the ratio of fusinite to semi-fusinite as conversion increased.

Overall, Martin Lake lignite showed a decrease in the most reactive components as conversion increased, which may explain why conversion slows down at 85-90%. The remaining residue is not totally unreactive, however, suggesting that higher conversion may be possible with the proper process or pretreatment.

INTRODUCTION

Work at Amoco and at the direct coal liquefaction pilot plant facility, operated by the Southern Company Services for the U.S. Department of Energy in Wilsonville, Alabama, has shown that typical conversion for Martin Lake, Texas lignite is in the range of 90-93% for two-stage liquefaction when the first stage reactor is opearated at about 825 °F. However, when supported hydrogention catalyst is used in the first stage, temperatures are kept below 810 °F to preserve catalyst activity. In these cases, coal conversion is only 85-90%. To identify the chemical and physical phenomena that underlie this low conversion, Martin Lake lignite and two of its residues, from runs at Amoco, were characterized using several analytical methods. Our main objective was to investigate the chemical and physical differences between the unreacted, unconverted Martin Lake lignite and converted residue samples after liquefaction. The specific objectives of this work were to find some reasonable answers to the questions of "what are the chemical functionalities involved in the liquefaction of low rank coals" and "why does conversion of low rank coals stop at 85-90% during catalytic/catalytic (C/C) liquefaction."

Three samples were used in this investigation, an unconverted Martin Lake lignite (0% conversion), a residue product from the low conversion process (64% conversion) and a residue product from the high conversion process (89% conversion). The samples were analyzed for elemental analysis (C, H, N, S, and O), proximate analysis (moisture, ash, volatile matter and fixed carbon), bulk

metals by Inductively Coupled Plasma (ICP) spectroscopy, surface minerals by X-ray Photoelectron Spectroscopy (XPS), Scanning Electron Microscopy (SEM), solid state ^{13}C NMR, and IR spectroscopy. Petrographic analysis was also performed.

EXPERIMENTAL

The two Martin Lake lignite residues were obtained from Amoco's AU-51L pilot plant and were the products of the two stage catalytic/catalytic (C/C) liquefaction process with Amocat-1C™ catalyst. Stage 1 and stage 2 process temperatures for low conversion residue were 100 and 740 °F and for the high conversion residue were 790 and 740 °F, respectively. Both residues and unconverted Martin Lake Lignite samples were washed with 40 volumes of THF prior to the analytical work.

The organic carbon, hydrogen and nitrogen content of the samples were measured by a Leco CHN-600 elemental analyzer. Total sulfur and oxygen content of the samples were determined using a Leco SC-132 sulfur analyzer and a Leco RO-478 oxygen determinator, respectively. The values for moisture, ash, volatile matter and fixed carbon of the samples were determined using a Perkin Elmer TGA 7 thermogravimetric analyzer.

The NMR data were obtained on a Chemagnetic M100 solid state NMR spectrometer operating at ^{13}C resonance frequency of 25.15 MHz. Cross-Polarization/Magic Angle Spinning (CP/MAS) technique was used to obtain solid state ^{13}C NMR spectrum. Based upon our previous studies of similar systems, cross-polarization contact time of 1 msec with 1 sec recycle delay were chosen as the best experimental parameters to obtain a quantitative ^{13}C spectrum. Dipolar Dephasing/Magic Angle Spinning (DD/MAS) technique was used to provide quantitative differentiation between quaternary and tertiary aromatic carbons. For the DD/MAS technique a period of 40 μsec was inserted between the end of the cross-polarization sequence and the beginning of the data acquisition, during which the high power proton decoupling field was turned off. In order to avoid linear phase distortions in the spectrum, rotational synchronized spin-echo procedure was used for both CP/MAS and DD/MAS techniques.

Diffused reflectance technique was used to obtain the IR data. Samples for diffuse reflectance infrared spectra were prepared by weighing 0.020 g sample and 0.980 g of KBr into a metal vial and shaking them for one minute on a Wig-L-Bug apparatus. The samples were transferred to the sample holder of a Harrick "Praying Mantis" diffuse reflectance apparatus. Spectra were obtained at 8 cm^{-1} resolution on a Mattson Cygnus 100 spectrometer using an MCT-A detector. A total of 1000 scans were co-added to obtain the final spectra.

A Perkin Elmer model 5400 Small Spot X-ray Photoelectron Spectrometer was used for XPS data collection. The data were obtained using an unmonochromatized radiation source from Mg K_α at 1253.6 ev on about 600 μm analysis area. The samples were pressed into pellets before analysis. The SEM data were obtained on a JEOL 840 A Scanning Electron Microscope equipped with a secondary and a Back Scatter Electron (BSE) detector. In addition, a TRACOR NORTHERN 5500 Energy Dispersive X-ray (EDX) system was used to obtain elemental composition of elements with atomic number of 11 or greater. The samples were prepared for SEM analysis by sprinkling them onto a sticky covered SEM stub and then coating them with AU/Pd (60/40) in vacuum evaporator. To expose cross sectional areas of the particles for detailed analysis, the samples were also embedded in a crystal bond compound and then grounded and polished before examination. SEM micrographs were obtained at 100, 500, and 5000 magnification. For microscopic examination of petrographic constituents, the samples were pelletized and polished according to the ASTM D 2797 procedure. The microscopic examinations were carried out at a magnification of 500 diameters, under oil immersion in reflected light illumination.

RESULTS AND DISCUSSION

Process conditions, percent conversion and product quality of Martin Lake lignite after liquefaction are shown in Table 1. Increasing the temperature of the first stage of the process from 100 to 740 °F, the lignite conversion (wt.%) was increased by more than 39% (from 64 to 89%). Most of this increase was in the lighter products such as C1-C3 and C4-360 °F distillate, which increased by 250%, and 360-640 °F distillate, which increased by more than 59%. The amount of product in the 650-975 °F range did not change significantly, and resid (975+ °F) was nearly eliminated.

Proximate analysis (wt.%, dry) and elemental analyses (wt.%, dry-ash-free) of the Martin Lake lignite and its two residues are shown in Table 2. As conversion of the lignite increased, a significant increase was observed in the ash content. This was followed by substantial decreases in the volatile matter (VM) and fixed carbon. Although oxygen content, determined by direct analysis, did not show a significant decrease with increasing lignite conversion, a considerable decrease was observed in the oxygen content calculated by difference, Table 2. The high values for direct oxygen of the residues reported here are believed to be distorted by the oxygen from the water present as moisture in these samples. In any case, the elemental oxygen data suggests a reduction in the oxygenated components during the process. As expected, the atomic H/C ratio was lower for the residue from the 64% converted sample (0.78) compared to the unconverted lignite (0.86). The atomic H/C ratio of the residue from the 89% converted sample, however, did not follow the same trend and increased (0.90). Although it is difficult to explain the increase in atomic H/C ratio, one explanation could be that some solvent is trapped in the residue from high conversion.

Solid state ^{13}C NMR data are shown in Table 3. The structural parameters, assuming 100 carbons per cluster, were derived by using combined CP/MAS and DD/MAS data following the method of Solum et. al[1]. In this procedure, linear integration over selected chemical shift ranges of the CP/MAS spectrum provides the relative concentration of different carbon types. Magic angle spinning generates high and low field spinning sidebands from SP^2 carbons. Sideband intensity is appropriately distributed for all SP^2 carbon types. The use of DD/MAS technique permits quantitative differentiation of protonated and bridgehead aromatic carbons. In the 40 μsec time period, for which the proton decoupling field is turned off, all the signal from protonated aromatic carbons is lost while quaternary aromatics lose only about 10% of their signal.[2] Thus, from the difference in aromatic band intensity between CP/MAS and DD/MAS spectra and accounting for 10% loss in intensity of quaternary carbons, relative concentration of protonated aromatic is calculated. Finally, simple mass balance provides the relative concentration of bridgehead aromatic carbons.

In general, solid state ^{13}C NMR data, in Table 3, indicate that as the lignite conversion increased, the carbon aromaticity increased and the carboxyl groups decreased. The size of condensed aromatic clusters is directly related to the ratio of bridgehead aromatic to ring aromatic carbons, i.e., the fraction of aromatic carbons in the bridgehead position.[1, 3] As an example, for the original lignite (0% conversion), the ratio of bridgehead carbons (12.7) to total ring carbons (54.9) is 0.23, which corresponds to an aromatic cluster slightly bigger than naphthalene. The same ratios for 64% and 89% conversion residues are 0.25 and 0.27, respectively, which corresponds to an aromatic cluster slightly smaller than anthracene. NMR data also indicated an increase in total SP^2 carbons, aromatic carbons, protonated and bridgehead carbons with increasing conversion. Although the data did not show any significant changes in substituted aromatic carbons with increasing conversion, there was a significant decrease in oxygenated functional groups. This clearly suggests that decarboxylation and reduction of phenols/ethers had taken place in the liquefaction process. It should be mentioned that the decrease in oxygenated functional groups was also seen in the data obtained from elemental analysis, IR and XPS spectroscopies.

The carbonyl and C-H stretch regions were analyzed using diffused reflectance IR spectroscopy. IR spectra for the original lignite (0% conversion) and the low conversion (64%) residue are shown in Figure 1. The specific band assignments are based on spectral information compiled by Painter

et al.[4-7] A comparison of spectra clearly shows that, while there is very little change in the C-H stretch region with treatment, there is clearly a loss in intensity for the bands in the 1740-1690 cm^{-1} region corresponding to oxygen-containing functional groups. Second derivative analysis of the spectra also indicates an intensity loss in the 1650-1560 cm^{-1} region, this loss is not obvious from the untreated spectra. While the bands near 1740 cm^{-1} and 1720-1690 cm^{-1} region may be attributed to an ester, ketone, aldehyde or carboxyl functional group, the bands in the 1650-1630 and ~1600 cm^{-1} are due to the highly conjugated C=O and highly conjugated hydrogen bonded C=O. The band at ~1600 cm^{-1} could also be attributed to aromatic ring breathing. The band in the 1590-1560 cm^{-1} is due to the carboxyl group in salt form (COO^-). Figure 2 compares the spectra for the original lignite (0% conversion) and the high conversion (89%) residue. In this case, a change in intensity of the C-H stretch band was seen. Of particular note are the relative decreases in intensity of the aliphatic CH_3 asymmetric stretch near 2960 cm^{-1} and aliphatic CH_2 and CH_3 symmetric stretch near 2850 cm^{-1}; and the increases in the intensity of aliphatic CH_2 and CH_3 asymmetric stretch near 2925 cm^{-1} and aromatic C-H stretch in the region of 3100-2990 cm^{-1}. Here again, the loss in the intensity of the bands corresponding to the loss of oxygen-containing functional groups can also be observed.

Surface composition (wt.%, relative) obtained by XPS and bulk metal composition obtained by ICP analyses are shown in Tables 4 and 5, respectively. The bulk analysis of the samples by ICP indicated that the major elements in the samples were Si, Fe, Al, Ca, Mg, Na, K and Ti. As was expected, the concentration of these elements increased as the lignite conversion increased. Two important pieces of information were obtained from XPS surface analysis. First, while the relative surface concentration (wt.%) for most of the elements (C, Si, Al, S, N, and Fe) did not change with increasing lignite conversion, the relative surface concentration of two elements (Ca and Mg) increased significantly with increasing conversion. There is some evidence in the literature that cations like Na^+, K^+ and Ca^{++} are inhibitors in coal pyrolysis[8, 9], but are promoter catalysts in coal steam gasification[10, 11]. Therefore, in coal liquefaction, it is possible that the increase in Ca and Mg at the surface of the reacting lignite particles slows down significantly, or stops, conversion at 85-90%. Second, the electron binding energies obtained from XPS show significant loss of oxygen-containing functional groups during the liquefaction process supporting the data from NMR and IR spectroscopy. Therfore, as the lignite conversion approaches 90%, the remaining residue is a highly aromatic material, hence the conversion slows down considerably.

Maceral compositions obtained from petrographic analysis are shown in Table 6. The data are presented on a mineral-matter-free basis to allow the comparison between the maceral groups vitrinite, inertinite and liptinite. The inertinite maceral group can be subdivided into fusinite, semifusinite, micrinite, macrinite and sclerotinite and the liptinite maceral group can be subdivided into sporinite, resinite and cutinite. Vitrinites and liptinites are considered to be the potentially most reactive macerals. Inertinites, on the other hand, are considered to be unreactive macerals with the exception of semifusinite which may be partially reactive. As expected, the vitrinite macerals (wt.%, mmf) decreased from 58.2 to 51.4 and then to 41.2 as the lignite conversion increased from 0% to 64% and to 89%, respectively. Liptinite macerals also showed the same trend, dropping from 10.0 for the original lignite to 3.5 for the 64% conversion residue and almost to zero (0.4%) for the high conversion residue. Decreases in vitrinite and liptinite macerals were offset by increases in inertinites. However, for the high conversion (89%) residue the relative increase in fusinite was much higher than the increase in semifusinite. This could mean that some of the semifusinite had reacted at high conversion conditions. Petrographic analysis indicated a significant increase in the mineral matter (13.9, 26.4, 52.4%) with increasing lignite conversion. This was expected, due to the disappearance of the reactive macerals with increasing conversion.

SEM also showed changes in morphology of the samples with increasing conversion. The sample from high conversion (85%) is composed of smaller and more porous particles than unconverted

or low conversion (64%) samples. Also, the unconverted and low conversion samples consisted of large organic particles decorated with mineral particles. Large organic particles are not seen in the high conversion sample; mineral and organic phases are intimately mixed.

SUMMARY AND CONCLUSIONS

The NMR data clearly suggests that the main structural transformations during liquefaction of Martin Lake lignite are aliphatic sidechain cracking, decarboxylation, and deoxygenation. Some of the NMR data from Table 3 are shown graphically in Figure 3 to suggest answers for the two questions asked earlier; "what are the chemical functionalities involved in the liquefaction of low rank coals" and "why does conversion of low rank coals stop at 85-90% during catalytic/catalytic (C/C) liquefaction." As the lignite conversion approaches 90%, aliphatic and carbonyl functional groups are depleted. The remaining residue is a highly aromatic material, therefore, the conversion slows down considerably. IR data confirmed the increase in aromatic C-H groups and decrease in aliphatic C-H functional groups. IR also indicated a significant loss of reactive carbonyl functional groups, which may cause slow conversion. Data from XPS analysis indicated that the relative surface concentration of two elements (Ca and Mg) increased significantly with increasing conversion, which could also decrease the reaction rate, and hence, reduce the conversion. The electron binding energies from XPS also showed a decrease in C-O and C=O functional groups during the liquefaction process. Petrographic analysis showed a significant decrease in the reactive macerals (vitrinites and liptinites), sharp increase in the unreactive macerals (inertinites) and partial conversion of semifusinite as conversion increased.

Overall, Martin Lake lignite showed a decrease in the most reactive components as conversion increased, which may explain why conversion slows down at 85-90%. The remaining residue is not totally unreactive, however, suggesting that higher conversion may be possible with the proper process or pretreatment.

REFERENCES

1. Solum. M. S., Pugmire, R. J., and Grant, D. M., Energy and Fuels, 3, 1989, 187.
2. Alemany, L. B., Grant, D. M., Pugmire, R. J., Alger, T. D., and Zilm, K. W., J. Am. Chem. Soc., 105, 1983, 2142.
3. Sethi, N. K., Facelli, J. C., Pugmire, R. J., and Grant, D. M., Analytical Chemistry, 60, 1988, 1574.
4. Painter, P. C., Coleman, M. M., Jenkins, R. G., and Walker, P. L., Jr., Fuel, 57, 1978, 125.
5. Painter, P. C., Coleman, M. M., Jenkins, R. G., Whang, P. W., and Walker, P. L., Jr., Fuel, 57, 1978, 337.
6. Painter, P. C., Snyder, R. W., Starsinic, M., Coleman, M. M., Kuehn, D. W., and Davis, A., Applied Spectroscopy, 35, 1981, 475.
7. Painter, P. C., Starsinic, M., and Coleman, M. M., "Determination of Functional Group in Coal by Fourier Transform Interferometry" in Fourier Transform Infrared Spectroscopy, Ferraro, J. R. andBasile, L. J., eds, vol. 4, 1985, Academic Press, N. Y.
8. Tyler, R. J., Fuel, 58, 1979, 680.
9. Tyler, R. J., and Schafer H. N., Fuel, 59, 1980, 487.
10. Hengel, T. D., and Walker, P. L., Jr., Fuel, 63, 1984, 1214.
11. Linares-Solano, A., Hippo, E. J., and Walker, P. L., Jr., Fuel, 65, 1986, 776.

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Table 1.

Process Conditions and Product Quality Data for Martin Lake Lignite

Conditions and Products	Lignite Conversion 0	64	89
Stage 1 Temperature, °F	Unreacted	100	790
Stage 2 Temperature, °F	Lignite	740	740
C1-C3, wt.%		3.4	10.1
C4-360 °F, wt.,%		3.9	13.7
360-650 °F, wt.%		24.4	38.8
650-975 °F, wt,%		8.8	9.5
975+ °F, wt.%		9.8	1.0
H_2 Consumption, wt.%		7.8	8.6

Table 2.

Proximate and Elemental Analyses Data Obtained for Martin Lake Lignite and the Converted Residues

	Lignite Conversion 0	64	89
Proximate Analysis (wt.%, dry)			
Moisture[a]	2.35	3.59	1.52
Ash	13.35	25.93	43.57
Volatile Matter	42.89	32.57	26.13
Fixed Carbon	43.76	41.50	30.30
Elemental Analysis (wt.%, dry-ash-free)			
Carbon	70.90	76.55	76.12
Hydrogen	5.11	5.03	5.76
Nitrogen	1.22	1.62	1.46
Sulfur	1.60	2.52	5.22
Oxygen (by difference)	21.17	14.28	11.44
Oxygen (direct)	21.76	18.20	17.98
H/C (atomic ratio)	0.86	0.78	0.90

[a]Moisture values are on as-recieved basis.

Table 3.

Solid State ^{13}C NMR Data for Martin Lake Lignite and the Converted Residues

Structural Parameters	Lignite Conversion 0	64	89
Carbon Types (total = 100)			
Total SP^2	64.1	73.3	80.3
-- Carbonyl	9.0	6.0	6.0
-- Ring Aromatic	54.9	66.7	73.8
* Phenolic/Ethers	9.7	9.4	8.9
* Protonated	19.8	25.9	29.1
* Substituted	12.8	14.9	15.9
* Bridgehead	12.7	16.6	19.9
Total SP^3	35.9	26.7	19.7
# Bridgehead / # Rings	0.23	0.25	0.27
# Carbons / Cluster	10	11	12

Table 4.

Surface Composition (wt.%, Relative) Data from XPS Analysis of Martin Lake Lignite and the Converted Residues

Lignite Conversion	O	C	Si	Al	S	N	Fe	Ca	Mg
0	30.4	52.0	8.1	5.6	0.4	0.9	1.0	0.7	0.9
64	24.0	57.1	8.2	4.7	0.1	1.2	0.8	1.9	1.7
89	24.7	55.8	7.3	5.2	0.4	1.0	1.0	2.5	1.8

Table 5.

Metal Composition (Wt.%) Data from ICP Analysis of Martin Lake Lignite and the Converted Residues

Lignite Conversion	Mg	Ca	Al	Si	Fe	Na	K	Ti	Sr
0	0.26	1.08	1.16	2.91	1.23	0.07	0.06	0.08	0.03
64	0.51	2.34	2.43	5.40	2.70	0.13	0.11	0.15	0.07
89	0.71	3.80	3.81	7.60	4.70	0.19	0.18	0.22	0.10

Table 6.

Maceral Composition Obtained from Petrographic Analysis of Martin Lake Lignite and the Converted Residues

	Lignite Conversion		
Macerals (wt.%, mineral-matter-free)	0	64	89
Vitrinites	58.2	51.4	41.2
Inertinites	29.2	44.3	58.4
* Fusinite	2.3	3.8	16.7
* Semifusinite	22.7	36.4	32.8
* Micrinite	2.6	3.3	7.6
* Macrinite	1.4	0.8	1.3
* Sclerotinite	0.2	0.0	0.0
Liptinite	12.6	4.3	0.4
* Sporinite	10.0	3.5	0.4
* Resinite	2.1	0.8	0.0
* Cutinite	0.5	0.0	0.0

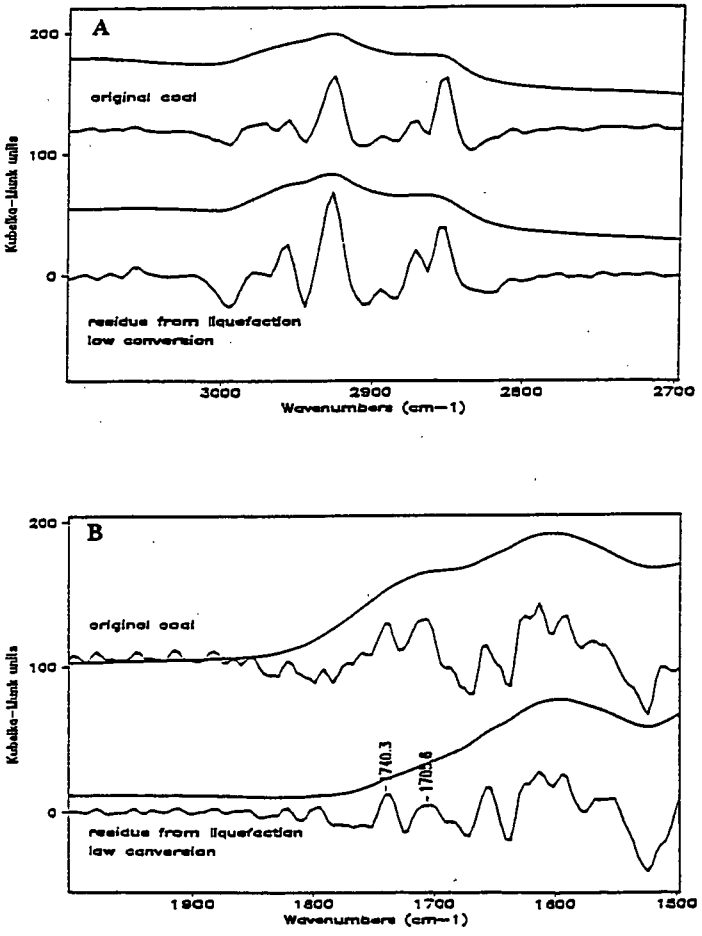

Figure 1. Infrared Spectrum for Martin Lake Lignite Coal and Low Conversion Residue. A) C-H Stretch; B) C=O Stretch.

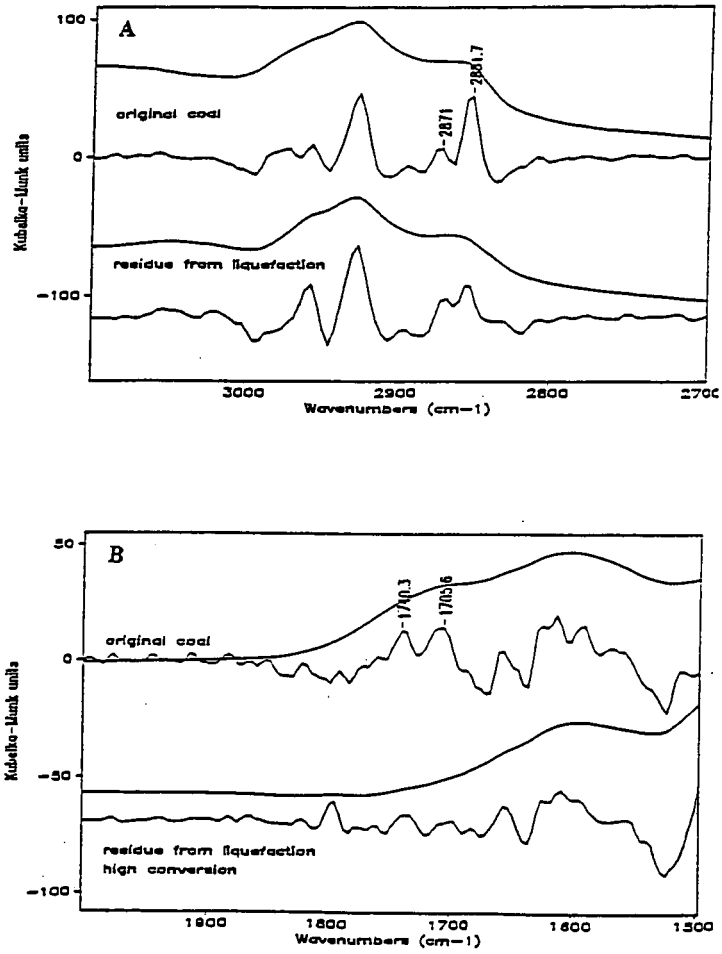

Figure 2. Infrared Spectrum for Martin Lake Lignite Coal and High Conversion Residue. A) C-H Stretch; B) C=O Stretch.

Figure 3. Carbon Types in Unconverted Martin Lake Lignite by C^{13} NMR